

198. *Unstable Intermediates. Part XXVIII.\* Solvated Electrons: Rigid Organic Solvents.*

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A variety of alcohols in the glassy state at 77°K have an intense absorption in the 550 m $\mu$  region after exposure to  $\gamma$ -radiation. This is rapidly bleached by visible light, and a single symmetrical electron resonance band at  $g = 2.001$ , having a width of about 14 gauss, is simultaneously lost. These results, reminiscent of those obtained with fluid ethanol and methanol exposed to high-energy electrons and with  $\gamma$ -irradiated aqueous glasses of alkali-metal hydroxides, are interpreted in terms of electrons trapped in well defined "holes" in the glass.

In contrast, various ethers in the glassy state have, after irradiation, an intense absorption band at about 1500 m $\mu$  which is associated with an electron resonance absorption again at  $g = 2.001$  but having a width of only 4 gauss.

Deuteration had no effect on the electron resonance except when the hydroxyl proton was involved; the band-width was then reduced to about 6 gauss. No colour, or only a very faint colour, was detected when the glasses were replaced by crystalline material.

CONTINUING our studies of "solvated"<sup>1</sup> and "trapped" electrons<sup>2,3</sup> we have returned to the problem of the violet colour which develops when primary and secondary alcohols are exposed to high-energy radiation at 77°K. The problem is of renewed interest in view of the recent detection of a transient species in electron-irradiated alcohols having an absorption band in the 600 m $\mu$  region and assigned to "solvated" electrons.<sup>4</sup> There is conflicting evidence concerning the nature of the coloured species in solid alcohols,<sup>2,5</sup> and one purpose of this work is to attempt to resolve this.

It has been stressed that the task of "solvating" electrons in fluid polar media is far smaller than that in solids,<sup>2</sup> and that much of the evidence for electrons trapped in rigid organic media is ambiguous since any impurity having relatively low-lying vacant molecular orbitals can act as an efficient trap, and many of the molecules used as sources of photoelectrons may also act as traps.<sup>2</sup>

The conclusion from a large number of electron resonance studies of irradiated non-ionic solids is that the final result, even at very low temperatures, is homolytic bond-fission rather than electron ejection and trapping.

However, it has recently<sup>6</sup> been observed that  $\gamma$ -irradiated alkyl iodides gave different products when in the glassy and crystalline states, and that an intense blue coloration developed only in the glass. Also, van Voorst<sup>7</sup> found that a band at 7700 cm.<sup>-1</sup> in glassy 2-methyltetrahydrofuran is associated with a narrow electron resonance band. These bands resulted when solutions of dinegative aromatic ions were exposed to ultraviolet light, their growth paralleling the loss of the dinegative ion and gain of the mononegative ion, as estimated from changes in the visible spectra. The dinegative ion was re-formed on bleaching with light having frequencies greater than about 16,000 cm.<sup>-1</sup>, and scavenger experiments with electron-acceptor molecules indicated that the concentration of trapping sites in 2-methyltetrahydrofuran was about 10<sup>-2</sup>M. Similar conclusions have been drawn<sup>8</sup> from changes in electronic spectra after irradiation with ultraviolet light and  $\gamma$ -rays.

\* Part XXVII, Hulme and Symons, preceding Paper.

<sup>1</sup> Catterall and Symons, *J.*, 1964, 4342.

<sup>2</sup> Symons, *J.*, 1963, 1189.

<sup>3</sup> Blandamer, Shields, and Symons, *J.*, 1964, 4352.

<sup>4</sup> Taub, Sauer, and Dorfman, *Discuss. Faraday Soc.*, 1963, **36**, 206.

<sup>5</sup> Symons, "Peroxide Reaction Mechanisms," ed. Edwards, Interscience, London, 1962, p. 137.

<sup>6</sup> Fenrick, Filseth, Hanson, and Willard, *J. Amer. Chem. Soc.*, 1963, **85**, 3731.

<sup>7</sup> van Voorst, Ph.D. Thesis, University of Amsterdam, 1963.

<sup>8</sup> Hamill, Guarino, Ronayne, and Ward, *Discuss. Faraday Soc.*, 1963, **36**, 169.

The second purpose of the present study was to compare the behaviour of ethers and alcohols in the glassy and crystalline states and to probe the physical nature of the trapping sites in these media by measuring their electron resonance and electronic spectra after irradiation and bleaching.

#### EXPERIMENTAL AND RESULTS

*Materials.*—These were highest grade available and were dried by standard procedures. In some instances solvents were thoroughly degassed prior to irradiation but this precaution did not significantly alter the results.

*Preparation of Glasses.*—Most solvents gave fairly clear glasses when rapidly cooled in liquid nitrogen. Diethyl ether glassified occasionally, but readily became polycrystalline when

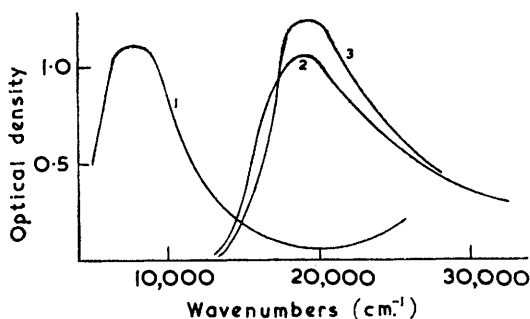


FIG. 1. Optical spectra of irradiated solvents at 77°K.

1. 2-Methyltetrahydrofuran.
2. Ethanol.<sup>14</sup>
3. Methanol.<sup>14</sup>

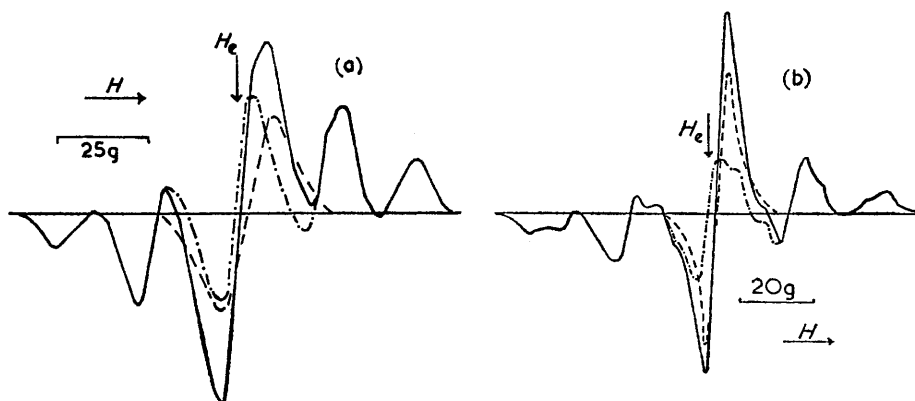


FIG. 2. First derivative of the electron spin resonance spectra of  $\gamma$ -irradiated ethanol at 77°K. (a) EtOH; (b) EtOD. — before bleaching; - - - after bleaching; - · - · -, difference curve assigned to trapped electrons.  $H_0$  is the field for which  $g = 2.0023$ .

cooled slowly. We were unable to obtain *t*-butyl alcohol in a glassy state, whereas acetone gave solids which appeared to consist of polycrystalline and glassy regions.

*$\gamma$ -Irradiation, Electron Resonance, and Electronic Spectra.*—These were carried out and obtained as described previously.<sup>3</sup>

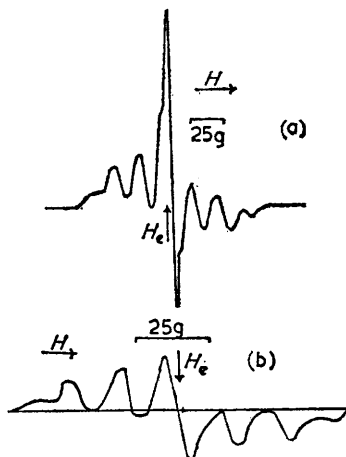
*Analysis of Electron Resonance Spectra.*—Typical spectra of  $\gamma$ -irradiated solids obtained before and after bleaching with visible light are given in Fig. 2. In many cases bleaching was accompanied by the loss of a single symmetrical band in the free-spin region which could be reconstructed by subtraction of the complex spectra before and after bleaching in the manner described for irradiated alkali-metal hydroxide glasses.

This subtraction was not possible for methanol glasses since the spectrum due to trapped organic radicals also changed in form during the bleaching process. An approximate result only could be obtained from the spectra of bleached and unbleached acetone since, on bleaching, the individual bands due to trapped organic radicals became narrower, even in the wings of the spectra.

Results obtained from these subtractions for alcohols and ethers, including deuterated ethanol, are given in Table 1.

*Effect of Crystallinity.*—Crystalline *t*-butyl alcohol and diethyl ether did not become coloured during irradiation and the characteristic central line was not observed in the electron resonance spectra. Partially crystalline acetone was blue in the glassy regions but apparently colourless in regions of crystallinity. These results are in accord with those<sup>6</sup> for irradiated ethyl iodide.

FIG. 3. Electron spin resonance spectra of  $\gamma$ -irradiated 2-methyltetrahydrofuran (a) before and (b) after bleaching.  $H_0$  is the field for which  $g = 2.0023$ .



In an attempt to study trapped electrons in a tertiary alcohol in the glassy state, we irradiated 1-methylcyclohexanol glass at 77°K. Unfortunately no violet colour developed, and there was no indication of an extra central line in the complex electron resonance spectrum.

TABLE 1.

Electron spin resonance data assigned to electrons trapped in  $\gamma$ -irradiated rigid organic solvents at 77°K.

Solvent	$g$ -Factor $\pm 0.0005$	$\Delta H_{MS}$ * (gauss)	Colour
Methanol ††	—	—	Violet
Ethanol	2.0010	$14 \pm 1$	Violet
EtOD	2.0013	$6 \pm 1$	Violet
Propan-2-ol §	2.0018	$12 \pm 1$	Violet
Acetone	$2.002 \pm 0.001$	$6-10$	Blue-black
Diethyl ether	2.0013	$3.4 \pm 0.5$	Blue-black
2-Methyltetrahydrofuran	2.0011	$4.2 \pm 0.5$	Blue-black
1,3-Dioxolan ¶	2.0018	$4.8 \pm 0.5$	Blue-black

\* Line-width between points of maximum slope of the absorption. † Polycrystalline methanol, *t*-butyl alcohol, *t*-pentyl alcohol, acetone, diethyl ether, 1,2-dimethoxyethane, and tetrahydrofuran remained colourless after prolonged irradiation and had spin-resonance spectra apparently free from the central line assigned to trapped electrons. ‡ 1-Methylcyclohexanol, benzyl alcohol, and cyclohexane glasses became yellow or brown on irradiation, but neither the colour nor the spin-resonance absorption was modified on exposure to visible light. § The colour centre was thermally destroyed at 100°K and the free radical from the parent alcohol at 115°K as evidenced by electron spin resonance measurements. ¶ The e.s.r. signal associated with the colour centre, but not the ether radical, was readily saturated by the microwave power.

Similarly, cyclohexanone gave a good glass, but the red-brown colour which developed on irradiation was unaffected by visible light.

*Effect of Added Salts.*—Samples of propan-2-ol containing  $10^{-1}M$  alkali-metal fluorides glassified at 77°K became intensely violet after exposure to  $\gamma$ -rays. This colour was readily bleached, and the electron resonance spectrum associated with the coloured species was indistinguishable from that obtained from pure propan-2-ol.

## DISCUSSION

*Evidence for Trapped Electrons.*—By “trapped” electrons we mean electrons which are not part of a single molecular entity. Thus, addition of an electron to, say, benzene

to give  $C_6H_6^-$  in the solid state would not constitute "trapping" in this sense. The phenomenon is closely linked to the concept of "solvated" electrons in fluid media,<sup>9</sup> but is not necessarily identical since the extent of orientational polarisation is likely to differ greatly in the solid and liquid states. The evidence in favour of the concept that the violet species in alcohols and the blue species in ethers are trapped electrons is as follows.

(1) There are single low-energy absorption bands having very high oscillator strengths and an asymmetry which is characteristic of *F*-centre and "solvated" electrons.<sup>9,10</sup> (2) For alcohols these bands are very close to that attributed to "solvated" electrons in fluid alcohols,<sup>4</sup> being shifted slightly to high energies as found for electrons in aqueous hydroxide glasses relative to aquated electrons.<sup>3,11</sup> (3) The colours are readily bleached and there is a corresponding loss of spin-resonance absorption. (4) The spin-resonance line attributed to the trapped electron has a *g*-factor close to 2.0010, which is the value found for "solvated" electrons and electrons in hydroxide glasses.<sup>3</sup> (5) The other products of photolysis of monoaromatic di-anions in rigid methyltetrahydrofuran, namely the corresponding anions, have been clearly identified by optical and spin-resonance spectroscopy. (6) Incorporation of electron acceptors suppresses the formation of these colour centres.<sup>12</sup>

This evidence is considerable, and in the remaining discussion this postulate is accepted. Evidence against the concept of electron-trapping in rigid alcohols has been discussed elsewhere<sup>13</sup> and is referred to in the ultimate section below.

*Nature of the Trapping Site.*—There is now good evidence that the colour centres are only formed in appreciable concentrations when glassy solids are used. These resemble the fluid state and contrast with the crystalline state in that they have a large number of vacancies or holes which presumably have volumes approximating to those of the solvent molecules. Added evidence in favour of the concept that electrons are trapped at such vacancies comes from the saturation effects observed by Alger and his co-workers<sup>14</sup> and by van Voorst.<sup>7</sup> The latter found, by the use of scavengers, that the concentration of such vacancies was about  $10^{-2}M$  in rigid methyltetrahydrofuran at 77°K.

Thus, we envisage that electrons are initially trapped at vacancies, presumably because a stationary wave can be established with a consequent reduction in kinetic energy. The surrounding molecules provide the required barrier, as well as stabilisation through electronic polarisation. The shallow traps found in ethers are thought to be of this form, but the traps in alcohols are clearly different. Thus, the spin-resonance line is considerably broadened by the hydroxyl proton, which must therefore be an intimate part of the trap, as found for electrons in hydroxide glasses. Also, the optical transition requires about twice the energy of that for electrons in ethers. If these transitions are crudely described as being  $1s \rightarrow 2p$  of a spherical well then this means that the well in alcohols is very much deeper than that in ethers.

These observations are both explained if the localised field for the electrons trapped at vacancies in alcohols is sufficiently powerful to reorient at least some of the OH bonds so as to stabilise the charge.

*Line-widths.*—On simple theory the band-width of the electronic absorption spectrum for trapped electrons is a measure of the range of cavities involved.<sup>15</sup> This can be represented by a term  $\Delta R$ , where  $R$  is the radius of an equivalent spherical well for which the  $1s \rightarrow 2p$  transition with  $R = R_{av}$  corresponds to the band maximum. Values for  $\Delta R$  estimated for half-height positions on the low-energy side of the spectra are given in Table 2. The significance of these results is that, although the bands in the infrared region for electrons in ethers have about the same width as those for electrons in alcohols, the

<sup>9</sup> Symons, *Quart. Rev.*, 1959, **13**, 99.

<sup>10</sup> Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.

<sup>11</sup> Blandamer, Catterall, Shields, and Symons, *J.*, 1964, 4357.

<sup>12</sup> Chachitry and Hayon, *Nature*, 1963, **200**, 60.

<sup>13</sup> Symons and Townsend, *J.*, 1959, 263.

<sup>14</sup> Alger, Anderson, and Webb, *J. Chem. Phys.*, 1959, **30**, 695; 1961, **35**, 49.

<sup>15</sup> Blandamer, Shields, and Symons, *J.*, to be published.

TABLE 2.

Band maxima and widths \* for the optical spectra assigned to trapped electrons together with spherical potential well radii ( $R_{\max}$ ) † and radial distribution ( $\Delta R$ ) deduced therefrom.

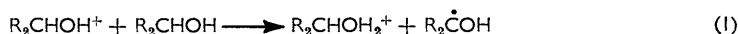
System	$\nu_{\max}$ . (cm. <sup>-1</sup> )	$R_{\max}$ .	$\Delta\nu/2$	$\Delta R$
MeOH <sup>14</sup> .....	19,400	4.03	2200	0.25
EtOH <sup>14</sup> .....	19,400	4.03	3200	0.38
Bu <sup>n</sup> OH <sup>14</sup> .....	19,900	3.98	4600	0.57
Bu <sup>t</sup> OH <sup>14</sup> .....	19,200	4.05	4600	0.59
2-Me-THF †§ .....	7500	6.48	2000	1.10
2-Me-THF <sup>7</sup> .....	8000	6.28	2000	0.96
10m-KOH in H <sub>2</sub> O § .....	17,000	4.30	3000	0.44

\* Half-width at half-height on low-energy side. † Calculated from  $h\nu = 1.04h^2/8mR^2$ . ‡ Salmon, *Discuss. Faraday Soc.*, 1963, **36**, 284. § Present work.

spread of cavity sizes is far greater. Furthermore, the range of sizes increases as the alkyl group R in alcohols ROH increases in bulk. These results are in good accord with predictions of the present theory. The problem will be discussed in more detail elsewhere.

*Fate of the Positive Radical-ion.*—In no instance have we obtained evidence for the ions  $R_2\dot{C}H\cdot OH^+$  in the spin-resonance spectra of irradiated alcohols. Indeed, residual spectra not assigned to trapped electrons closely resemble those assigned to radicals  $R_2\dot{C}OH$  formed by reaction with photolysed hydrogen peroxide.<sup>16,17</sup> This interpretation has been strongly supported by recent results for these radicals in fluid solution, where assignment is unambiguous.<sup>18</sup>

Accordingly, we postulate the reaction:



though some  $R_2\dot{C}OH$  is probably formed by direct loss of hydrogen atoms. Similar reactions probably occur for ethers, but no attempt will be made to interpret the poorly resolved spectra obtained.

It is noteworthy that an  $\alpha$ -proton is involved in reaction (1) and that we have not been able to detect trapped electrons in irradiated tertiary alcohols. It may be that secondary reactions such as (1) are necessary in order to prevent an efficient back-reaction.

*Spectra of  $R_2\dot{C}OH$  Radicals.*—Low-intensity violet colours result when dilute solutions of hydrogen peroxide in rigid primary or secondary alcohols are photolysed, and these have been assigned to the radicals  $R_2\dot{C}OH$  detected by electron resonance.<sup>19</sup> Attempts to reconcile this point of view with results for  $\gamma$ -irradiated alcohols have been made,<sup>5,13</sup> but the present considerations certainly outweigh them.

Nevertheless, the arguments in favour of the postulate that radicals  $R_2\dot{C}OH$  have a forbidden transition in the 500 m $\mu$  region are strong,<sup>5</sup> and it is possible that an unfortunate coincidence has confused the issue.

A major point in the original argument in favour of the concept that radicals  $R_2\dot{C}OH$  have a weak absorption band in the 500 m $\mu$  region was that no such band could be detected in photolysed peroxide-tertiary alcohol glasses. Unfortunately, we have also been unable to detect bands associated with trapped electrons in any tertiary alcohol after exposure to  $\gamma$ -rays. Thus, this ambiguity remains.

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<sup>16</sup> Gibson, Symons, and Townsend, *J.*, 1959, 269.

<sup>17</sup> Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.

<sup>18</sup> Dixon and Norman, *J.*, 1963, 3119.

<sup>19</sup> Symons and Townsend, *J. Chem. Phys.*, 1957, **25**, 1299.